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(54) **HUILE POUR TRANSFORMATEUR**
(54) **TRANSFORMER OIL**

(57) A transformer oil comprises a base stock and a non- unsaturated, unsubstituted compound having at lest one hydrogen donor.



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ABSTRACT OF THE DISCLOSURE

A transformer oil comprises a base stock and a non-unsaturated, unsubstituted compound having at lest one hydrogen
5 donor.

Title: TRANSFORMER OIL

FIELD OF THE INVENTION

This invention relates to oils for use in transformers.

5

BACKGROUND OF THE INVENTION

Conventional transformer oils are typically manufactured from vacuum gas oil fractions derived from naphthenic crudes and in particular light naphthenic distillates. 10 (~60N). Although transformer oils made from naphthenic crudes perform adequately, they suffer from poor biodegradability and ecotoxicity. Paraffinic crudes, hydroprocessed oils and synthetic fluids such as poly-alpha-olefins and others are more environmentally friendly and less toxic. Paraffinic crudes and synthetics also exhibit 15 enhanced oxidative and electrical properties. Therefore, they would be preferred basis for the manufacture of transformer oils.

Unfortunately, it has not been possible to formulate transformer oils using such base stocks because they do not perform adequately in the ASTM D2300b hydrogen gassing test. 20 Commercially available naphthenic transformer oils exhibit negative hydrogen gassing tendencies whereas paraffinic, hydroprocessed and synthetic based transformer oils exhibit positive hydrogen gassing values. Consequently naphthenic based transformer oils are currently preferred because in the event that 25 hydrogen is evolved due to electrical stress they would tend to absorb the evolved hydrogen thus reducing the chances of an explosion.

DESCRIPTION OF THE INVENTION

30 It has now been discovered that is possible to manufacture transformer oils from base stocks comprising paraffinic crudes, hydrocracked oils and from synthetics with enhanced hydrogen gassing properties through the addition of an

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additive. In terms of its chemical structure, the general class of additives that are effective at improving (i.e. lowering) the hydrogen gassing value are hydrogen donor molecules, that is, compounds which incorporate within them labile hydrogen atoms.

5 Surprisingly, purely aromatic compounds such as naphthalene do not effect the hydrogen gassing value. Accordingly, the additive may be any compound which is a hydrogen donor other than a pure aromatic compound , i.e. a non-unsaturated, unsubstituted compound.

10 Examples of such compounds include dihydrophenanthrene, phenyl ortho xylyl ethane, Agent 791TM (alkylated benzene), Dowtherm RPTTM (tetrahydro-5-(1-phenylethyl)-naphthalene, Mobil MCP 917TM (alkylated naphthalene), acenaphthene, tetrahydronaphthalene and, tetrahydroquinoline.
15 Preferably, such compounds are selected from the group consisting of acenaphthene, tetrahydronaphthalene and tetrahydroquinoline.

Without being limited by theory, it is believed that in use transformer oils are subject to high electrical stresses which cause bonds to break in the transformer oil base stock. Without the
20 hydrogen donor additive of the invention, hydrogen is evolved from the transformer oil. In the presence of the additive, the availability of hydrogen from the additive causes alternate compounds to form and thus reduce the amount of hydrogen which is evolved from the transformer oil.

25 These hydrogen donor molecules may be added to the base oil in amounts from 0.1 to 10 wt. % based on the weight of the transformer oil, preferably from about 1 to 2 wt. %.

Since only a small amount of the additive is required, the additive itself does not have a significant negative effect on the
30 human and eco-toxicological properties of the inherently good human and eco-toxicological properties of paraffinic, hydrocracked and synthetic fluids.

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Additionally, the addition of the hydrogen gas suppressing additive to paraffinic, hydroprocessed and synthetic base stocks does not have a negative impact on other physical, chemical and electrical attributes of the electrical fluid.

5 Fluids used in the preparation of transformer oils can be made using a variety of hydroprocessing technologies that are described in the literature. Hydroprocessing or hydrotreating involves the contacting of a hydrocarbon feedstock. Paraffinic feedstocks (i.e., those possessing a predominant amount of normal
10 and iso-paraffins) are preferred since they respond well to hydroconversion. Thus paraffinic feedstocks possessing the appropriate physical attributes such as density, aromatics content, viscosity and volatility are contacted with a catalyst at elevated temperatures and pressures in a hydrogen gas atmosphere. The
15 hydroprocessing conditions are adjusted to effectuate the conversion of polynuclear aromatics to smaller hydrogenated species, as well as the elimination of sulphur and nitrogen molecules. Typical hydroprocessing conditions are temperatures of 300 - 425°C, pressures of 600 - 4000 psig and liquid hourly space
20 velocities of 0.1 to 5.0 hr⁻¹. Catalyst used in the hydrotreating step include those based on sulfided group VIB and VIII metals.

 Additionally, the hydrotreated product can be treated over a hydroisomerization rare earth catalyst for the purpose of converting the normal paraffins to iso-paraffins which has the
25 benefit of lowering the pour point of the oil.

 As a last step the hydrotreated or the sequentially hydrotreated - hydroisomerized oil can be finished by passing the oil over a hydrogenation catalyst at thermodynamically favorable conditions. Typically these conditions include high pressures (600
30 to 4000 psig) and temperatures lower than those used during the hydrotreating or hydroconversion step (220 - 330°C). Catalyst used in the hydrogenation step include those based on noble metals as

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well as those based on sulfided group VIB and VIII metals.

Example 1

5 A series of hydrogen donor additives were added to
 phoenix N65DW™ to form a transformer oil. Phoenix N65DW™ is
 a base stock prepared by the sequential hydrotreatment,
 hydroisomerization and hydrogenation and subsequent
 atmospheric and vacuum distillation of a paraffinic vacuum
 10 bottoms feedstock. The test employed for the initial screening was
 the ASTM D2300B gassing test. The amount of the additive and the
 gassing level are set in Table 1.

TABLE 1

15

List of additives and Gassing Values

Feedstock:		N65DW (657-0812)	
	Additive	D2300B	Additive Concentration, wt%
		Gassing Value, microL/min	
20	None	51.7	0
	Voltesso 35 (657-1207)	-17.7	-
	Acenaphthene	-6	1
	Acenaphthene	3.7	0.5
	Acenaphthalene (contains several % Acenap	-2	1
	Tetrahydronaphthalene	-36.8	1
25	Tetrahydroquinoline	-13.8	1
	Dihydrophenanthrene	27.8	1
	Phenyl ortho xylyl ethane	35.2	2
	Agent 791 (alkylated Benzene)	46.7	1
	Dowtherm RP (Tetrahydro-5-(1-phenylethyl) -naphthalen	38.9	1
	Alkylated Naphthalene Mobil MCP 917	39.2	1
	Alkylated Naphthalene Mobil MCP 917	40.2	1

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The gassing tendency of Voltesso 35™ (a commercially available transformer oil) was tested to be -17.7 µL/min. As it is evident from Table 1 some of hydrogen donor type molecules, (i.e. the partially hydrogenated molecules) had a significant effect on suppressing gassing while the purely aromatic molecules did not have an impact. This is a very interesting result since it was always assumed that good gassing performance was purely a function of the aromatics level. The compounds which performed best were acenaphthene, and tetralin. Addition of 1 to 2% of these compounds produced level gassing performance which approached or actually depressed below that observed with Voltesso 35™.

Example 2

Two fully formulated oils were prepared and tested to determine whether they met the Ontario Hydro and the US ASTM 3239 requirements. One electrical oil was made with 2% tetralin in N65DW™ and the other was composed of a 1% acenaphthene in 50/50 mixture of N65DW™ and HT60™. HT60 is a paraffinic high saturates white oil prepared by the sequential hydrotreating - solvent dewaxing - hydrogenation of a narrow cut paraffinic gas oil fraction. Solvent dewaxing is used to reduce the level of normal paraffins and as a consequence to lower the pour point of the oil. The only other ingredients added to the oils were 0.08 wt. % DBPC™ and 0.07 wt. % Agent 27™ (Pearsol 100) pour point depressant. Results of the study are shown in Table 2.

TABLE 2

Sample ID	Inspection	Ontario Hydro Specifications CSA C90-1978	ANSHASTM ASTM D 3487	Reported VOLTEISO 35	Measured VOLTEISO 35 687-1297	MSLOW - 7% Temple 687-1864	MSLOW / HTM - 7% AgassidHem 687-1868	MSLOW
PPD, Pearled 100 wth (Agass 27)						3.07	0.07	
DEPC Inhibitor Content, wt%		0.08 max				3.08	0.08	
Physical Inspections								
Colour, ASTM	D1500	1.0 max	0.5 max	<0.5	<0.5	0	0	
Viscosity, 100C, cSt	D445		3.0 max	2.2				2.4
Viscosity, 40C, cSt	D445	10 max	12.0 max	6.3		6.49	9.83	6.87
Viscosity, 0C, cSt	D445	75 max	78 max	50	43.56	41.93	51.87	
Viscosity, -40C, cSt	D445	6000 max		2000		1261.6	2723.5	
Density, 15C	D1298	0.905 max	0.91 max	0.899	0.8714	0.8422	0.831	0.8298
Pour, C	D87	.45 max	.40 max	.40		4.54	.48	.38
Interfacial Tension, N/m	D871	35 min	40 min	46		46	44.6	
Flash, C	D82	146 min	143 min	158	152	168	182	182
Sulphur, wt%	D1275	nd		nd		-	-	-
Corrosive Sulphur	D874		non corrosive					
Copper Corrosion	D130				16	16	16	
Water Content, ppm	D1533		35 max	25 max		0	0	
TAN, mg KOH/g	D874	0.03 max	<0.01	<0.01	0.06	0.06	0.06	
Sediment, wt%	D2007			78				
Aniline Point, C	D811		63 - 64	80	76.3	99	100.5	
Gelling Tendency @60C, g/Anin	D2308		<30	30 / 4 Unvot 60	-17.2	-36.4	-7.6	48.2
Dielectric Breakdown Voltage @60Hz								
Disc Electrodes	D877	30 min	30 min	46	45	50	41	
VOE Electrodes, 1V	D1816		25 min	32 - Unvot 60		37	42	
Dielectric Breakdown Voltage@25C								
Impulse Strength, 1V	D3300		143 min	170		262	298	
Power Factor @ 60Hz, %								
100C	D824	0.5 max	0.3 max	0.25		0.007		
25C			0.05 max	0.003 - Unvot 60		0.001	0.02	
Oxidation Stability								
Rotary Bomb, min	D2112			180"		180	180	
DD440, 24h								
Visual Sludge	D2440	nd		nd		nd	nd	
TAN, mg KOH/g		0.15 max		0.05		<0.01	<0.01	
DD440, 64h								
Visual Sludge	D2440			0.11	0.05	<0.01	<0.01	
TAN, mg KOH/g				0.25	0.19	<0.01	<0.01	
DD440, 168h								
Visual Sludge	D2440		0.3 max	0.13 - Unvot 60		<0.01	<0.01	
TAN, mg KOH/g			0.5 max	0.35 - Unvot 60		<0.01	<0.01	

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As it can be seen, both formulations easily met all of the important physical property requirements. In addition 24 hour, 64 hour and 164 hour D2440 oxidation test results were either similar to or better than the results reported for Voltesso 35™.

- 5 There also appears to be significant performance benefits over Voltesso 35™ in many of the dielectric tests.

The gassing performance was -26.6 µL/min for the tetralin case and -7.6 µL/min for the acenaphthene case.

10 **Example 3**

- To simulate a plant trial, two 4.1kV pad transformers were chosen. One unit was drained of Voltesso 35™, flushed and re-filled with 135 gallons of test fluid, while the other unit was drained
15 and re-filled with 135 gallons of fresh Voltesso 35™.

- The test fluid was prepared using VHV12 as a base stock. VHV12 is a severely hydrogenated and hydroisomerized oil, prepared by the sequential hydrotreatment, hydroisomerization and hydrogenation and subsequent atmospheric and vacuum
20 distillation of a paraffinic vacuum bottoms feedstock. 0.08 wt. % DBPC antioxidant and 2 wt. % of tetrahydronaphthalene (the anti-gassing additive) were added to the base stock. Prior to its use the test fluid was 'dried' by means of sparging with nitrogen gas for a period of about 1-hour. This had the effect of reducing the water
25 content from > 50 ppm to < 35 ppm (which is standard for most electrical oils), while at the same time increasing the dielectric power factor to >40kV. The physical properties of the finished product are shown in Table 3.

TABLE 3

			<u>Specifications</u>	
			<u>CSA Class B</u>	<u>ASTM</u>
5	<u>Inspections</u>	<u>658-0598</u>		
	Anti-Gassing Additive, %	1.94		
	DBPC, %	0.074		
	VHVI 2 (970510)	97.986		
	Density, 15C, kg/L	D4052 0.8718	0.906	0.91
	Viscosity@100C, cSt	D445 2.35		
10	Viscosity@40C, cSt	D445 8.186	12 max	12 max
	Viscosity@-40C, cSt	D445 1627	6000 max	
	Pour, C	D97 -45	-40 max	-40 max
	Flash, C, COC	D92 166	145 min	145 min
	Colour	D1500 <0 5	0.5 max	0.5 max

15

The condition of the transformer unit was evaluated every few weeks. The evaluation included routine gas analysis and electrical test, D2300 hydrogen gassing tendency, and D2440 oxidation stability (@76h & 164h).

20

The electrical loading and performance of two transformers was continuously monitored. Analysis of the data indicates that the two transformers operated 'normally' over the period of the test run.

The gassing results are shown in Table 4. The results show that gassing tendency of the test fluid is significantly lower than Voltesso 35™ and that, the gassing values remained relatively constant over time. Additionally, the results suggest that the concentration of the anti-gassing additive can be reduced from 2 wt. % to a lower value.

30

Results of the 76 hour and 164 hour D2440 tests are shown in Table 5. As expected, the oxidation stability of the test fluid is exceptionally good. In fact it is so good that it passes the

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CSA/ASTM oxidation requirements for uninhibited and inhibited electrical oils which can contain up to 0.4% DBPC. Electrical oils containing 0.08 wt. % and less DBPC are considered to be uninhibited. Conversely, Voltesso 35 only meets the oxidation requirements for uninhibited oils.

The biodegradability of the fully formulated test electrical oil was evaluated using the standard OECD 301B test. The result of the 28-day test was 60%, which signifies that it can be classified as readily biodegradable.

TABLE 4

Gassing Tendency of Test Fluid

Date	08-Jun-98	30-Jun-98	05-Aug-98	02-Sep-98
	08-Jun-98	30-Jun-98	05-Aug-98	02-Sep-98
Sample #	658-0764	658-0840	658-0949	658-1044
Gassing Tendency, microL/min	-41.2	-46	-37.3	-51.6

Gassing Tendency of Voltesso 35 Electrical Fluid

Date	08-Jun-98	30-Jun-98	05-Aug-98	02-Sep-98
Sample #	658-0765	658-0839	658-0950	658-1045
Gassing Tendency, microL/min	-11	-11.7	-12	-11.9

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TABLE 5

D2440 Oxidation Stability Of Test Fluid

5

		Specifications			
		CSA		ASTM 3487	
		Uninhibited	Inhibited	Uninhibited	Inhibited
Date	Initial				
	02-Jun-98 08-Jun-98 30-Jun-98 05-Aug-98 02-Sep-98				
Sample #	658-0598 658-0764 658-0840 658-0949 658-1044				
72 hours					
	Sudge, wt%				
Total Acids, mgKOH/g	<0.01 0.01	0.1 max 0.4 max		0.15 max 0.50 max	0.10 max 0.30 max
164 hours					
	Sudge, wt%				
Total Acids, mgKOH/g	<0.01 0.01	0.2 max 0.5 max	0.05 max 0.2 max	0.30 max 0.60 max	0.20 max 0.40 max

D2440 Oxidation Stability of Voltesso 35 Electrical Fluid

Date	08-Jun-98 30-Jun-98 05-Aug-98 02-Sep-98
Sample #	658-0765 658-0839 658-0950 658-1045
72 hours	
	Sudge, wt%
Total Acids, mgKOH/g	0.02 0.11
164 hours	
	Sudge, wt%
Total Acids, mgKOH/g	0.08 0.08 0.08 0.12 0.26 0.26 0.27 0.36

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THE EMBODIMENTS OF THE INVENTION IN WHICH AN
EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE
DEFINED AS FOLLOWS:

5

1. A transformer oil comprising:
 - (a) a base stock; and,
 - (b) a non-unsaturated, unsubstituted compoundhaving at least one hydrogen donor.

10

2. The transformer oil as claimed in claim 1 wherein the base stock is prepared from paraffinic crude oil, hydrocracked oil, synthetic oil or a mixture thereof.

15

3. The transformer oil as claimed in claim 1 wherein the non-unsaturated, unsubstituted compound is a substituted aromatic compound.

20

4. The transformer oil as claimed in claim 3 wherein the substituted aromatic compound is naphthalene or quinoline.

25

5. The transformer oil as claimed in claim 1 wherein from about 0.1 to about 10% of the non-unsaturated, unsubstituted compound is added.

30

6. A process for reducing the hydrogen gas evolved from a transformer oil comprising adding a non-unsaturated, unsubstituted compound having at least one hydrogen donor to the transformer oil.

7. The process as claimed in claim 6 wherein the transformer oil is prepared from paraffinic crude oil, hydrocracked

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oil, synthetic oil or a mixture thereof.

8. The process as claimed in claim 6 wherein the non-
unsaturated, unsubstituted compound is a substituted aromatic
5 compound.

9. The process as claimed in claim 8 wherein the
substituted aromatic compound is naphthalene or quinoline.

10 10. The process as claimed in claim 6 wherein from about
0.1 to about 10% of the non-unsaturated, unsubstituted compound
is added.

15